

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C21C 1/10, C22C 33/08	A1	(11) International Publication Number: WO 95/24508 (43) International Publication Date: 14 September 1995 (14.09.95)
(21) International Application Number: PCT/NO95/00029 (22) International Filing Date: 13 February 1995 (13.02.95) (30) Priority Data: 940819 9 March 1994 (09.03.94) NO (71) Applicant (for all designated States except US): ELKEM A/S [NO/NO]; Nydalsveien 28, N-0483 Oslo (NO). (72) Inventor; and (75) Inventor/Applicant (for US only): SKALAND, Torbjørn [NO/NO]; Hellemyrbakken 101, N-4628 Kristiansand (NO). (74) Agent: VINDENES, Magne; Elkem a/s, P.O. Box 40, Vågsbygd, N-4602 Kristiansand (NO).		(81) Designated States: BR, JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: CAST IRON INOCULANT AND METHOD FOR PRODUCTION OF CAST IRON INOCULANT (57) Abstract The invention relates to an inoculant for the manufacture of cast iron with lamellar, compacted or spheroidal graphite wherein said inoculant comprises between 40 and 80 % by weight of silicon, between 0.5 and 10 % by weight of calcium and/or strontium and/or barium, less than 4 % by weight of aluminium, 0-10 % by weight of manganese and/or titanium and/or zirconium, between 0.5 and 10 % by weight of oxygen in the form of one or more metal oxides, the balance being iron. The invention further relates to a method for producing an inoculant for the manufacture of cast iron with lamellar, compacted or spheroidal graphite, providing a base alloy comprising 40 to 80 % by weight of silicon, 0.5 to 10 % by weight of calcium and/or strontium and/or barium, less than 4 % by weight of aluminium, 0-10 % by weight of manganese and/or titanium and/or zirconium, the balance being iron, and adding 0.5 to 10 % by weight of oxygen in the form of one or more metal oxides to the base alloy.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

Title: Cast iron inoculant and method for production of cast iron inoculant.

5 Technical Field:

The present invention relates to a ferrosilicon based inoculant for the manufacture of cast iron with lamellar, compacted or spheroidal graphite and to a method for production of the inoculant.

10 Background Art:

Cast iron is typically produced in a cupola or induction furnaces, and generally has about 2 to 4 percent carbon. The carbon is intimately mixed in with the iron and the form which the carbon takes in the solidified cast iron is very important to the characteristics of the cast iron. If the carbon takes the form of iron carbide, then the
15 cast iron is referred to as white cast iron and has the physical characteristics of being hard and brittle which in certain applications is undesirable. If the carbon takes the form of graphite, the cast iron is soft and machinable and is referred to as gray cast iron.

20 Graphite may occur in cast iron in the lamellar, compacted or spheroidal forms and variations thereof. The spheroidal form produces the highest strength and most ductile form of cast iron.

The form that the graphite takes as well as the amount of graphite versus iron carbide,
25 can be controlled with certain additives that promote the formation of graphite during the solidification of cast iron. These additives are referred to as inoculants and their addition to the cast iron as inoculation. In casting iron products from cast iron, the foundryman is continually plagued by the formation of iron carbides in thin sections of the cast. The formation of the iron carbide is brought about by the rapid cooling of
30 the thin sections as compared to the slower cooling of the thicker sections of the cast. The formation of iron carbide in a cast iron product is referred to in the trade as "chill". The formation of chill is quantified by measuring "chill depth" and the power of an inoculant to prevent chill and reduce chill depth is a convenient way in which to measure and compare the power of inoculants.

35

There is a constant need to find inoculants which reduce chill depth and improve the machinability of gray and ductile cast irons.

Since the exact chemistry and mechanism of inoculation and why inoculants function as they do is not completely understood, a great deal of research goes into providing the industry with a new inoculant.

5 It is thought that calcium and certain other elements suppress the formation of iron carbide and promote the formation of graphite. A majority of inoculants contain calcium. The addition of these iron carbide suppressants is usually facilitated by the addition of a ferrosilicon alloy and probably the most widely used ferrosilicon alloys are the high silicon alloy containing 75 to 80 % silicon and the low silicon alloy
10 containing 45 to 50 % silicon.

U.S. patent No. 3,527,597 discovered that good inoculating power is obtained with the addition of between about 0.1 to 10 % strontium to a silicon-bearing inoculant which contains less than about 0.35 % calcium and up to 5 % aluminium.

15

It is further known that if barium is used in conjunction with calcium the two act together to give a greater reduction in chill than an equivalent amount of calcium.

The suppression of carbide formation is associated by the nucleating properties of the inoculant. By nucleating properties it is understood the number of nuclei formed by
20 an inoculant. A high number of nuclei formed improve the inoculation effectiveness and improves the carbide suppression. Further a high nucleation rate may also give better resistance to fading of the inoculating effect during prolonged holding time of the molten iron after inoculation.

25

Disclosure of Invention:

It has now been found that the addition of oxygen in the form of metal oxide to ferrosilicon based inoculants containing calcium and/or strontium and/or barium substantially increases the nucleation rate of the inoculant.

30

According to a first aspect the present invention relates to an inoculant for the manufacture of cast iron with lamellar, compacted or spheroidal graphite wherein said inoculant comprises between 40 and 80 % by weight of silicon, between 0.5 and 10 % by weight of calcium and/or strontium and/or barium, less than 4 % by weight of
35 aluminium, 0 - 10 % by weight of manganese and/or titanium and/or zirconium, between 0.5 and 10 % by weight of oxygen in the form of one or more metal oxides, the balance being iron.

According to a first embodiment, the inoculant is in the form of a solid mixture of a ferrosilicon based alloy and the metal oxide.

5 According to a second embodiment the inoculant is in the form of a ferrosilicon based alloy containing the metal oxide.

The inoculant according to the present invention preferably comprises 0.5 to 5 % by weight of manganese and/or titanium and/or zirconium.

10 According to a preferred embodiment the metal oxide is selected among FeO, Fe₂O₃, Fe₃O₄, SiO₂, MnO, MgO, Al₂O₃, TiO₂ and CaSiO₂.

The oxygen content of the inoculant is preferably between 1 and 6 % by weight.

15 It has surprisingly been found that the inoculant according to the present invention increases the number of nuclei formed when the inoculant is added to cast iron, thus obtaining an improved suppression of iron carbide formation using the same amount of inoculant as with conventional inoculants, or obtaining the same iron carbide suppression using less inoculant than when using conventional inoculants.

20 According to a second aspect the present invention relates to a method for producing an inoculant for the manufacture of cast iron with lamellar, compacted or spheroidal graphite, comprising providing a base alloy comprising 40 to 80 % by weight of silicon, 0.5 to 10 % by weight of calcium and/or strontium and/or barium, 0 - 10 % by weight of manganese and/or titanium and/or zirconium, less than 4 % by weight of aluminium, the balance being iron, and adding 0.5 to 10 % by weight of oxygen in the form of one or more metal oxides to the base alloy.

25 According to one embodiment of the method the metal oxides are mixed with the base alloy by mechanical mixing of solid base alloy particles and solid metal oxide particles. The mechanical mixing can be carried out in any conventional mixing apparatus which gives a substantially homogeneous mixing, such as for example a rotating drum.

30 According to another embodiment of the method the metal oxides are supplied to a melt of the base alloy whereafter the melt is solidified. The metal oxides are preferably added to the stream of molten base alloy when pouring the alloy into casting moulds. Alternatively the metal oxides may be added in the casting moulds before pouring molten base alloy into the moulds.

EXAMPLE 1**Production of inoculant.**

- 5 Four batches of 7000 grams of 75 % ferrosilicon having a particle size between 0.2 and 1mm and containing about 1 % by weight of calcium, 1 % by weight of barium and 1 % by weight of aluminium were mechanically mixed with different amount of powderous iron oxide materials as shown in table 1. The mixing was carried out using
- 10 a combined tilting and rotating drum to obtain homogeneous mixtures of the different inoculants. The oxygen content of the four produced inoculants A through D is also shown in table 1.

Table 1

15

Test mixture No.	Oxide		Total oxygen content in the mixture.
	Type	Weight (g)	
A	Fe ₂ O ₃	350	1.4 wt %
B	Fe ₂ O ₃	700	2.7 wt %
C	Fe ₂ O ₃	1400	5.0 wt %
D	Fe ₃ O ₄	613	2.3 wt %

EXAMPLE 2

- 20 The four inoculants A through D produced in example 1 were used for inoculation of a cast iron containing 3.7 % by weight of carbon, 2.4 % by weight of silicon, 0.1 % by weight of manganese 0.025 % by weight of phosphorus, 0.005 % sulphur and 0.050 % by weight of magnesium. For comparison purposes two tests were made using a conventional base inoculant containing 75 % ferrosilicon, 1 % by weight of calcium, 1 % by weight of barium and 1 % by weight of aluminium. In each test 0.3
- 25 % by weight inoculant was added to the cast iron melts. After casting nodule densities in 5 mm sections of the castings were determined. The results are shown in table 2. Heat No. 1 and 2 refer to tests with the conventional inoculant, while heat No. 3 - 6 in table 2 refer to tests with inoculants A through D according to table 1 in example 1.

Table 2

Heat No.	Inoculant	Nodule density (mm ⁻²)
1	(Ca, Ba, Al) - FeSi	381
2	(Ca, Ba, Al) - FeSi	370
3	(Ca, Ba, Al) - FeSi + Fe ₂ O ₃ (A)	477
4	(Ca, Ba, Al) - FeSi + Fe ₂ O ₃ (B)	624
5	(Ca, Ba, Al) - FeSi + Fe ₂ O ₃ (C)	427
6	(Ca, Ba, Al) - FeSi + Fe ₃ O ₄ (D)	449

- 5 As can be seen from table 2 the inoculants according to the present invention give an increased nodule density compared to the conventional inoculant of up to about 70 %.

EXAMPLE 3

- 10 Production of inoculant.

Four samples of 7000 grams of a conventional inoculant based on 75 % ferrosilicon and containing 1 % by weight of calcium, 1 % by weight of barium and 1 % by weight of aluminium were melted in a graphite crucible using an induction furnace.

- 15 Small amounts of calcium and barium were added to the liquid alloy to adjust for fading of these elements during melting and holding. The different melts were poured into copper chill moulds while adding various types and amounts of iron oxides to the metal stream and/or to the chill moulds prior to casting. Table 3 gives a summary of the inoculants produced giving the type and amount of iron oxide added and the final
- 20 chemical composition of the inoculant.

Table 3

Heat No.	Oxide Type Added	Oxide Weight Added	Chemical Composition of Inoculant Alloys Produced (in wt %)				
			% Si	% Ca	% Ba	% Al	% O
E	Fe ₂ O ₃	400 g	73.9	0.61	0.84	0.78	1.83
F	Fe ₃ O ₄	400 g	75.6	0.86	0.95	0.88	1.84
G	Fe ₃ O ₄	633 g	70.2	1.05	1.18	0.84	3.60
H	FeO	785 g	68.1	1.15	1.30	0.94	5.70

5

The produced inoculants E through H were subsequently crushed and sieved, and the 0.2 - 1.0 mm fraction of each material were used for cast iron inoculation trials as described in example 4.

10 **EXAMPLE 4**

The four inoculants E through H produced in sample 3 were used for inoculation of a cast iron containing 3.7 % by weight of carbon, 2.4 % by weight of silicon, 0.1 % by weight of manganese, 0.025 % by weight of phosphorus, 0.005 % sulphur and 0.050 % by weight of magnesium. For comparison purposes one test was made using a conventional base inoculant containing 75 % ferrosilicon, 1 % by weight of calcium, 1 % by weight of barium and 1 % by weight of aluminium. In each test 0.3 % by weight inoculant was added to the cast iron melt. After casting nodule densities in 5 mm sections of the casting were determined. The results are shown in table 4. Heat No. 1 refer to the test with the conventional inoculant, while heat No. 2 - 5 in table 4 refer to tests with inoculants E through H according to table 3 in example 3.

Table 4

Heat No.	Inoculant	Nodule density (mm ⁻²)
1	(Ca, Ba, Al) - FeSi	375
2	(Ca, Ba, Al) - FeSi + Fe ₂ O ₃ (E)	552
3	(Ca, Ba, Al) - FeSi + Fe ₃ O ₄ (F)	524
4	(Ca, Ba, Al) - FeSi + Fe ₃ O ₄ (G)	525
5	(Ca, Ba, Al) - FeSi + FeO (H)	454

- 5 As can be seen from table 4, an increase in nodule density of up to about 50 % was obtained by the inoculants according to the present invention compared to the nodule density obtained by the conventional inoculant.

CLAIMS

- 5
1. An inoculant for the manufacture of cast iron with lamellar, compacted or spheroidal graphite wherein said inoculant comprises between 40 and 80 % by weight of silicon, between 0.5 and 10 % by weight of calcium and/or strontium and/or barium, less than 4 % by weight of aluminium, 0 - 10 % by weight of manganese and/or titanium and/or zirconium, between 0.5 and 10 % by weight of oxygen in the form of one or more metal oxides, the balance being iron.
- 10
2. Inoculant according to claim 1, characterized in that it is in the form of a solid mixture of a ferrosilicon based alloy and the metal oxide.
- 15
3. Inoculant according to claim 1, characterized in that it is in the form of a ferrosilicon based alloy containing the metal oxide.
- 20
4. Inoculant according to claims 1 - 3, characterized in that the metal oxide is selected among FeO, Fe₂O₃, Fe₃O₄, SiO₂, MnO, MgO, Al₂O₃, TiO₂ and CaSiO₂.
- 25
5. Inoculant according to claims 1 - 4, characterized in that the oxygen content is between 1 and 6 % by weight.
- 30
6. Inoculant according to claims 1 - 5, characterized in that the inoculant comprises between 0.5 and 5 % by weight of manganese and/or titanium and/or zirconium.
- 35
7. A method for producing an inoculant for the manufacture of cast iron with lamellar, compacted or spheroidal graphite, providing a base alloy comprising 40 to 80 % by weight of silicon, 0.5 to 10 % by weight of calcium and/or strontium and/or barium, less than 4 % by weight of aluminium, 0 - 10 % by weight of manganese and/or titanium and/or zirconium, the balance being iron, and adding 0.5 to 10 % by weight of oxygen in the form of one or more metal oxides to the base alloy.
8. Method according to claim 7, characterized in that the metal oxides are mixed with the base alloy by mechanical mixing of solid base alloy particles and solid metal oxide particles.

9. Method according to claim 7. characterized in that the metal oxides are supplied to a melt of the base alloy whereafter the melt is solidified.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 95/00029

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C21C 1/10, C22C 33/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C21C, C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A2, 0232042 (ELKEM METALS COMPANY), 12 August 1987 (12.08.87), page 11, line 25 - line 50, claims 1-16 --	1-9
A	EP, A1, 0524444 (SKW TROSTBERG AKTIENGESELLSCHAFT), 27 January 1993 (27.01.93), claims 1-3 -- -----	1-9

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

1 June 1995

Date of mailing of the international search report

22 -06- 1995

Name and mailing address of the ISA/

Swedish Patent Office

Box 5055, S-102 42 STOCKHOLM

Facsimile No. +46 8 666 02 86

Authorized officer

Johan von Döbeln

Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/NO 95/00029

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A2- 0232042	12/08/87	SE-T3- 0232042	
		AU-A- 6786587	30/07/87
		CA-A- 1300894	19/05/92
		DE-A- 3773952	28/11/91
		JP-C- 1778127	28/07/93
		JP-B- 4056082	07/09/92
		JP-A- 62180010	07/08/87
		SU-A- 1813113	30/04/93
		US-A- 4666516	19/05/87
		US-A- 4749549	07/06/88
EP-A1- 0524444	27/01/93	DE-C- 4124159	09/04/92
		US-A- 5209901	11/05/93